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Tin-doped indium oxide films for highly flexible transparent conducting electrodes

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ABSTRACT

With the recent growing interest in flexible electronics, many studies are being conducted on flexible transparent conducting electrodes (TCE) such as Ag nanowires, Ag nanomeshes, carbon nanotubes, and graphenes. However, it will take time for such technologies to replace Sn-doped In_2O_3 (ITO), which is now widely used, due to challenges with reliability, mass-production, cost, and industry infrastructure. In this study, ITO films with different thicknesses were deposited on a flexible polymer substrate to investigate their optical and electrical properties and flexibility as a function of film thickness. Regardless of thickness, the ITO films' transmittance was about 80% at ~550 nm wavelength. The sheet resistances of all films were below 100 Ω/sq although resistance increased with decreasing film thickness. As a result of bending tests, it was found that thinner films had a higher threshold against bending strain. The sheet resistances did not significantly change above a bending radius of ~5 mm. In particular, the 50 nm-thick ITO film endured to a bending radius of ~3 mm, showing that it is a viable transparent electrode for flexible optoelectronics.

1. Introduction

Optoelectronic products such as flat panel displays, touch screen panels (TSP), solar cells and interactive electronics are increasingly popular and in demand [1–3]. The functionality of each of those devices is based on the use of a transparent conducting electrode (TCE) film. To meet performance requirements the electrically conductive thin film needs to be fabricated with materials that have low sheet resistance (R_s < 300 Ω/sq) and high light transmittance (T), preferably with a T greater than or equal to about 80% in the visible light region [4]. In addition to these two properties, an additional performance requirement, flexibility, has recently become important, due to the growing interest in flexible and wearable optoelectronics [5–8].

Tin-doped indium oxide (Sn-doped In_2O_3, ITO) is a degenerated n-type semiconductor with a wide band gap [9]. ITO exhibits a very low R_s (<200 Ω/sq) and high T (>80%) when it is conventionally deposited on glass substrates with substrate heating (>200 °C) [10–12]. As a result, it has been the most widely used TCE material in nearly all rigid optoelectronics for several decades [9–13]. With the recent growing interest in flexible electronics, ITO films are now also being deposited on flexible polymer substrates such as polycarbonate (PC) and polyethyleneterephthalate (PET), and their electrical properties, optical properties and flexibility have been investigated [14–16]. The results of these studies have demonstrated that ITO can successfully achieve R_s and T values suitable for commercial devices on polymer substrates, but flexibility is still lacking. While ITO film is being used commercially in curved display TVs and smart-watches, no bendable or wearable optoelectronic devices employing ITO have yet been commercialized [16–20]. According to published reports, the R_s of ITO drastically changes below R10, which corresponds to a bending radius of 10 mm [17,18]. This means that ITO film flexibility is limited to conditions above R10.

In addition to these reported shortcomings of ITO for flexible electronics, it is widely assumed that ITO is unsuitable for use in flexible and wearable devices because it is a ceramic, and consequently highly brittle. These previous reports of ITO's disadvantages have given rise to a highly motivated search for ITO alternatives, and those efforts have focused on candidates including Ag nanowires (NWs), metal-meshes, carbon nanotubes (CNT) and graphenes, PEDOT:PSSs, and their hybrids. A great number of studies on those alternative materials have been conducted worldwide and promising results been reported in many cases [21–24]. For instance, it has been reported that Ag-NWs and metal-meshes exhibit very low R_s (<100 Ω/sq) with moderate transmittance (>80%) and high flexibility. Carbon materials, conducting

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polymers and others have also shown the optimal electrical and optical properties (R_s < 1 kΩ/sq and transmittance > 80%) required for optoelectronics. However, nanowires and metals tend to be expensive, and are not suitable for mass production in low cost applications because they are also often scarce, and their fabrication procedures are complicated. Regarding CNTs and graphenes, their material properties are very sensitive to fabrication process conditions, which can result in high junction resistance and out-of-plane resistance, respectively, and at present, they are still not cost-effective. Conducting polymers are also limited by chemical and thermal instability. Therefore, in spite of the attractive opto-electrical and flexible properties of the various candidates, it is likely that these alternative technologies will still require a significant amount of development time before they are ready to replace ITO films in commercial applications [25]. Accordingly, further research on approaches to develop ITO for flexible electronics seems reasonable and necessary.

In this work, we prepared ITO films as coatings with different thicknesses for a systematic study on their properties in relation to flexibility. Specifically, the films were deposited on polymer substrates using room temperature sputtering, and their R_s, T and flexibility were investigated.

2. Experimental procedure

The ITO films were deposited on ~100 μm-thick PET substrates with by dc magnetron sputtering using an ITO commercial ceramic target (In_2O_3:SnO_2 = 90:10 wt%). The deposition was intentionally conducted at room temperature. A constant dc power of 500 W under Ar—O_2 mixture gases (Ar: 100 cm^3/min and O_2: 1 cm^3/min) and a working pressure of 3 mTorr was used. The thickness of the ITO films was controlled by sputtering time. The sputtering time was varied from 60 s to 150 s. Four ITO films with different thicknesses (~50 nm, ~69 nm, ~100 nm and ~124 nm) were fabricated. Their thickness was checked using an alpha-step surface-profile measuring system. Hereafter, the films are accordingly denoted as ITO50, ITO69, ITO100 and ITO124, respectively.

The crystal structures of the ITO films were evaluated by Grazing Incidence X-ray Diffraction (GI-XRD). GIXRD is known to be the best way to avoid an intense signal from the substrate and to obtain a stronger signal from the film [26]. The surface morphology of the ITO films was analyzed using Atomic Force Microscope (AFM). The as-deposited films were subjected to bending tests carried out with a custom-built bending tester. Surface images of the ITO films were checked after the bending-tests using a Scanning Electron Microscope (SEM).

The sheet resistance (R_s) of the ITO films was measured at room temperature with a 4-point probe electrical tester, as a function of film thickness before and after the bending test. The transmittance (T) and haze of the ITO films were measured at the 550 nm wavelength with a haze meter.

3. Results and discussion

After the ITO films were deposited on the PET-substrates, GI-XRD measurements of the films were conducted in order to evaluate the crystallinity of the films. Fig. 1 shows the XRD spectra of the films with thicknesses ranging from 50 nm to 124 nm, respectively. In Fig. 1a (2θ range: 20–70°), there appear to be no peaks corresponding to crystallized ITO (bixbyite crystal-structure). However, upon close examination of the patterns between 25–44° (Fig. 1b), a couple of small peaks corresponding to ITO were detected for both ITO100 and ITO124. The peak indexed at around 30° is known to be the main peak of ITO, which is the (222) plane. The intensities of the peaks, however, were very small, as can be seen, which means that the deposited films had poor crystallinity. This is because the energy needed to form crystalline ITO is not available when ITO is deposited on a polymer substrate at room temperature.

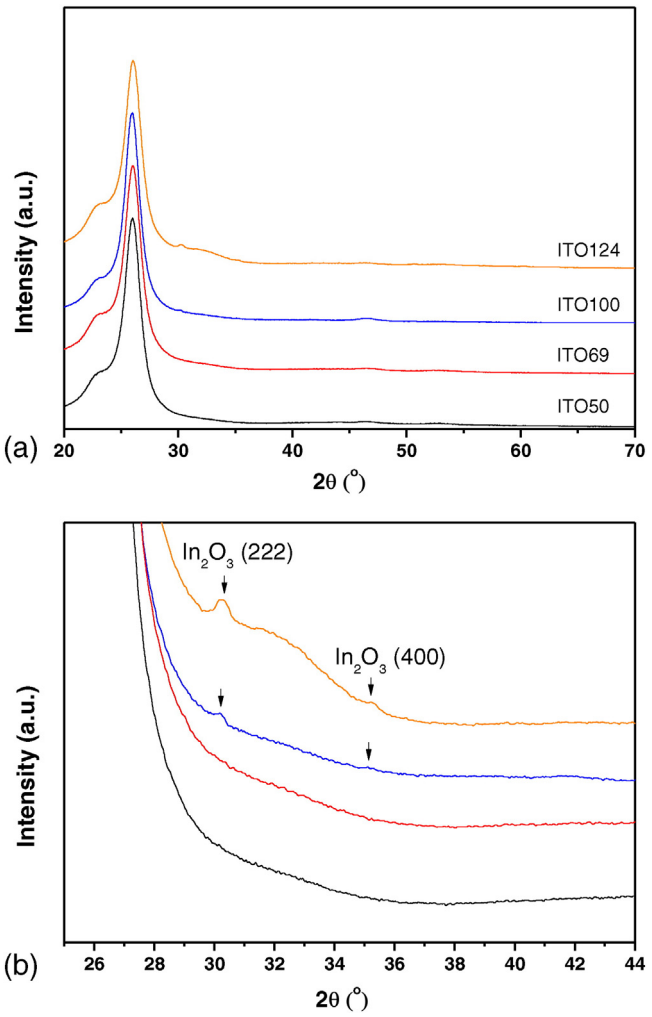

Fig. 1. (a) The XRD patterns of ITO films deposited on PET substrates with different thicknesses. (b) The XRD patterns of 25 ~44° were enlarged. Peaks corresponding to In_2O_3 were detected in ITO100 and ITO124, respectively.

No distinguishing peaks at all were observed in ITO69 and ITO50, indicating that ITO crystallinity became worse with reduced thickness. In order to determine how good or bad the films' crystallinity was, the lattice constant and distortion factor of the films were estimated using the indexed peaks. In general, it is known that the poorer the crystallinity is, the larger the lattice constant becomes [27]. According to a previous report, the lattice constant of a well crystallized ITO film was ~1.013 nm, and it showed very high peak-intensity (note that the ideal lattice constant of pure In_2O_3 is 1.012 nm (JCPDS, 06-0416)) [27]. As for the ITO100 and ITO124 prepared in this study, the calculated constants were ~1.025 nm and ~1.024 nm, respectively, which is larger than that of the reported ITO film. Lattice distortion was also observed to be 1.34% and 1.27% for ITO100 and ITO124, respectively, showing that crystallinity was reduced as the film thickness decreased. Lattice distortion is defined as $\Delta d/d_{hkl}$, where $\Delta d = d_{experiment} - d_{hkl}$ and d_{hkl} is the unstrained d-spacing of indium oxide (refer to the previous report for details) [27]. Based on the peak intensity, lattice parameter and distortion results, it is likely that the films prepared in this study were not well crystallized. Additionally, the crystallite size (or grain size) of ITO124 was estimated to be ~17 nm from the Scherrer equation with the peak corresponding to the (222)-plane [28].

The surface morphologies of the ITO films were studied by AFM. Fig. 2(a), (b), (c) and (d) show AFM images of the films over a scan area of 5 × 5 μm^2. Based on the AFM observations, the rms roughness (R_q) and average roughness (R_a) of the various films were estimated